Unusual Spectral Behavior of Charge-Density Waves with Imperfect Nesting in a Quasi-One-Dimensional Metal

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Low-temperature electronic properties of the charge-density-wave system $NbSe_3$ are reported from angle-resolved photoemission at 15 K. The effect of two instabilities $\mathbf{q}_1$ and $\mathbf{q}_2$ on the k-resolved spectral function is observed for the first time. With a pseudogap background, the gap spectra exhibit maxima at $\Delta_1^* \sim 110$ meV and $\Delta_2^* \sim 45$ meV. Imperfectly nested sections of the Fermi surface lack a Fermi-Dirac edge, and show the signature of a dispersion that is modified by self-energy effects. The energy scale is of the order of the effective gap $2\Delta_2^*$. The effect disappears above T_2, suggesting a correlation with the charge-density-wave state.

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The occurrence of charge-density waves (CDWs) in one-dimensional (1D) metals, as well as their impact on the electronic structure, is the object of intense research [1–3]. Effects under study include the destruction of the Fermi surface as well as the fluctuation-induced pseudogap above the transition temperature [4,5]. Essential for an understanding of the electronic effects is the determination of the CDW energy gaps. In real quasi-1D materials with coupling to the remaining dimensions, nesting conditions and the associated gap will vary across the Fermi surface. The gapping may even be incomplete, with parts of the Fermi surface still metallic. A case in point is the multiband Peierls system $NbSe_3$ which undergoes two CDW transitions but remains metallic down to the lowest temperatures [6,7]. $NbSe_3$ exhibits two incommensurate CDWs with transitions at $T_1 = 145$ K and $T_2 = 59$ K, below which the Fermi surface is drastically reduced [6]. Previous gap determinations on $NbSe_3$ have been performed by means of tunneling spectroscopy [8–10]. However, those data are averaged over the Brillouin zone (BZ) and cannot give an accurate account of the k-dependent gap spectra.

In addition, the existence of residual metallic bands in the low-temperature phase should allow a study of mass renormalization effects near the Fermi level. They originate from a strong coupling of the electrons to phonons (as expected in CDW systems) or other excitations available in the system. Such phenomena are particularly well accessible with angle-resolved photoemission spectroscopy (ARPES) and have only recently been observed on selected metallic surface states [11,12]. The existence of such quasiparticle renormalizations, however, has to date not been addressed experimentally in 1D CDW systems.

In this Letter, we report the first low-temperature k-resolved measurements of CDW effects on the electron bands in $NbSe_3$. ARPES data taken at $T = 15$ K provide an account of the excitation gaps Δ_1^* and Δ_2^* in the low-temperature phase at coordinates of optimum nesting. Though these spectra represent energy gaps induced by band backfolding, they deviate from a simple gap behavior. Non-nested parts of the Fermi surface do not show a conventional Fermi edge. The electronic dispersion exhibits the signature of self-energy effects on the energy scale of the full gap $2\ \Delta_2^*$.

Experimentally, vapor-transport grown $NbSe_3$ whiskers were cleaved at 15 K in ultrahigh vacuum. ARPES was performed at beamline 10.0.1 at the Advanced Light Source in Berkeley, equipped with a Scienta 2002 electron analyzer. Angular resolution corresponded to $\delta k \sim 0.006$ Å^{-1}, the total energy resolution was set to $\delta E \sim 25$ meV. Accurate calibration of $k_\perp$ is achieved via photon energy scans through various high-symmetry points of the BZ.

The Fermi surface of $NbSe_3$ is known from density-functional theory (DFT) [13]. Nesting of either CDW occurs between pairs of bands in the Fermi surface. Zone boundaries induced by the $\mathbf{q}_1$ CDW have recently been observed by ARPES in the fluctuation regime [13]. The summary of nesting conditions in Fig. 1(a) shows a Fermi surface cross section in the YΓZ plane, where Γ-Z is the 1D direction. Bands 2 and 3 are nested pairwise with $\mathbf{q}_1 = (0, 0.241, 0)$ (in units of reciprocal lattice constants). Nesting vector $\mathbf{q}_2 = (0.5, 0.259, 0.5)$ is directed along the space diagonal of the BZ, nested between bands 1 and 4. Its projection is indicated in Fig. 1(a). Perpendicular to this plane the dispersion is negligible.

The $\mathbf{q}_1$ CDW is nested along and near Γ-Z where the pair of bands 2 and 3 is degenerate, as shown in the angle scan at $T = 15$ K in Fig. 1(b) (plotted as negative second energy derivative $-d^2I/dE^2$ for better contrast). At the

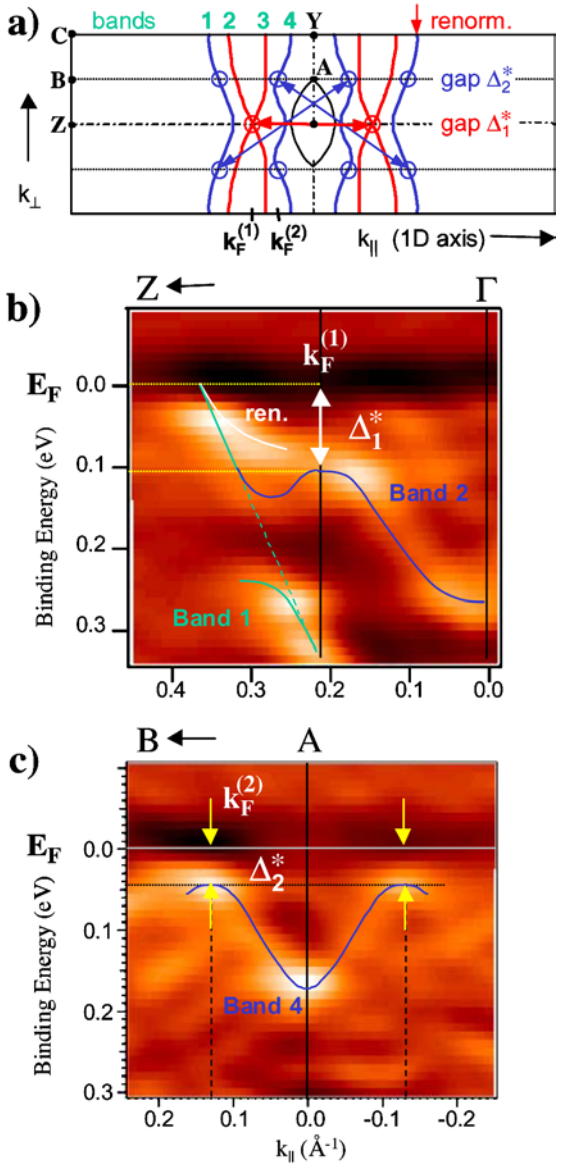

FIG. 1 (color online). (a) Schematic of the Fermi surface [13] with nesting vectors and observation conditions for energy gaps. For $\mathbf{q}_2$ the projection is shown. (b) Band map along Γ-Z at $T = 15$ K, displayed as $-d^2I/dE^2$ ($h\nu = 52.1$ eV). Backfolding at $q_1/2$ is observed, giving rise to an effective gap parameter Δ_1^*. (c) Observation of the $\mathbf{q}_2$-induced gap spectrum along A-B at $T = 15$ K ($h\nu = 34.7$ eV).

Fermi vector $k_F^{(1)} = q_1/2 = 0.22$ Å^{-1}, the band turns over as a result of CDW Bragg scattering and forms excitation gap Δ_1^*. At $k > q_1/2$, the backfolded band 2 couples to band 1, and a hybridization gap occurs. This refines the room temperature description in [13]. Near E_F, we observe indication of quasiparticle renormalization discussed in detail below.

The nesting of vector $\mathbf{q}_2$ and the corresponding excitation gap Δ_2^* is expected on a line A-B halfway between the high-symmetry lines of Fig. 1(a). The band map in Fig. 1(c) displays the result for the inner band 4 which provides the better observation condition, since the counterpart band 1 is affected by the aforementioned hybridization. Band backfolding is observed at $k_F^{(2)} = 0.13$ Å^{-1} in good agreement with the DFT calculation.

Those energy spectra taken at nested wave vectors k_F where backfolding occurs are identified as spectral functions of the respective energy gaps, as compiled in Fig. 2. The low-temperature spectra do not display well-defined energy gaps, instead, pseudogap behavior is observed with the spectral weight continuously decreasing towards E_F. An influence from extrinsic k broadening is unlikely. Surface effects are negligible for van der Waals bonded layered materials. Extrinsic defect scattering can be excluded since the quasiparticle features in our momentum distribution curves are relatively sharp. We therefore conclude that the pseudogaps are *intrinsic* properties of the single-particle spectra in the CDW phase. A mechanism that generates intensity in the gap region is the occurrence of quantum fluctuations in the low-temperature ordered phase [14,15]. Beyond theoretical treatments of ideal 1D cases, we also point out that the imperfectly nested Fermi surface may cause additional interactions that contribute to the gap spectral function.

An energy scale of the CDW effect on the spectral function is provided by the minimum binding energy of

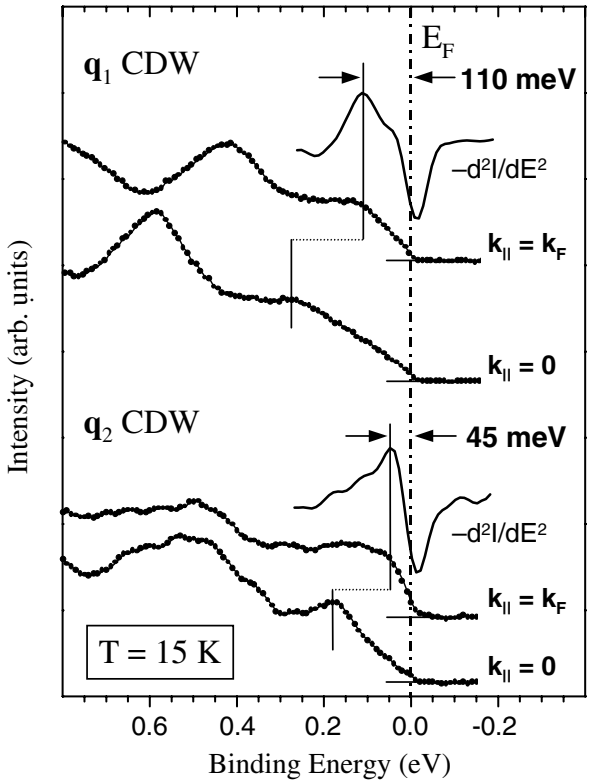

FIG. 2. Spectral functions from ARPES line scans at $k_\parallel = 0$ and at k_F for the effective gap parameters Δ_1^* and Δ_2^*. Gap spectra identified by backfolding are inherently broad and are complemented with second derivatives $-d^2I/dE^2$.

the dispersive peak in the presence of backfolding. The $-d^2I/dE^2$ display in Fig. 2 aids in such determination. In view of the pseudogap situation noted as effective gap parameter, we obtain values of $\Delta_1^* = 110 \pm 20$ meV and $\Delta_2^* = 45 \pm 10$ meV for the $\mathbf{q}_1$ and $\mathbf{q}_2$ CDW, respectively. The ratio $\Delta_2^*/\Delta_1^* \sim 0.4$ reflects the temperature ratio T_2/T_1. We caution that the underlying *quasiparticle* gap may actually be smaller, as shifts of spectral weight to higher binding energy can occur due to phonon satellites [16]. From tunneling spectroscopy with similar spectral shapes reported gaps are $\Delta_1^* = 85$ meV [8], $\Delta_1^* = 101$ meV [9], and $\Delta_2^* = 35$ meV [9,10]. The slightly larger ARPES gaps are in good agreement with these numbers, bearing in mind that tunneling averages over k space which will lead to an underestimation of the gap. Optical measurements to our knowledge have not covered a sufficient energy range yet [17].

Non-nested parts of the Fermi surface are accessed at the Y-C line, where the outermost band 1 extends up to the Fermi level yet does not match a CDW nesting condition. This is reflected in the 15 K spectra of Fig. 3 where band 1 shows up as the peak rapidly dispersing from 0.4 eV towards E_F, while no backfolding is observed. However, the intensity at the Fermi level is rather low, and a Fermi-Dirac edge is not observed. Theoretical models for such pseudogap behavior provide interpretation as either a true pseudogap due to quantum fluctuations of the order parameter alluded to above [14,15] with the caveat of an imperfectly nested Fermi surface or as the much debated signature of the destruction of the Fermi liquid in low dimensions.

Additionally, a low energy shoulder near E_F is observed, which close to the Fermi vector overlaps with the main peak. It displays a much reduced dispersion. Following the leading edge of the shoulder from k_F to smaller wave vectors, its energy saturates at $\sim 90 \pm 10$ meV. Our band calculations cannot provide an explanation for the shoulder feature.

What may be the origin of such dispersive behavior? In principle, two mechanisms are conceivable: (i) hybridization of bands resulting from CDW backfolding effects, and (ii) a genuine self-energy effect near the Fermi level. Hybridization would be possible with the neighboring band 2 when backfolded with $\mathbf{q}_1$. However, the zone

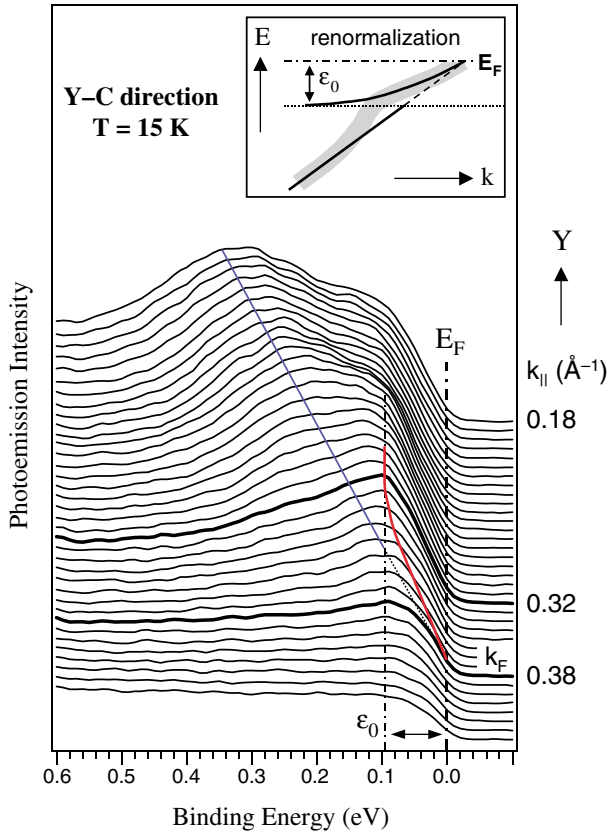

FIG. 3 (color online). Raw spectra of band 1 along Y-C at $T = 15$ K ($h\nu = 47.2$ eV). Close to the main branch (straight line), a shoulder near E_F is split off and forms a peak that saturates at ~90 meV. At lower k values, other bands begin to contribute intensity. The inset depicts mass renormalization in an energy window ε_0 and the associated shift of spectral weight (gray shaded line).

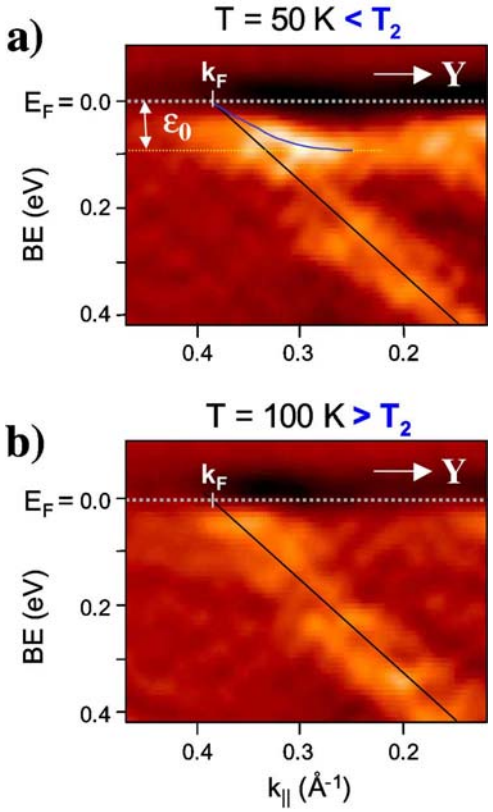

FIG. 4 (color online). Temperature dependence of the renormalized dispersion along Y-C (displayed as $-d^2I/dE^2$). (a) Slightly below the CDW transition temperature T_2, the mode is still present. (b) Above T_2 and still well below T_1, the coupling is no longer detected.

center data of Fig. 1(b) indicate that the shoulder is a separate phenomenon. Also, we observe that the effect disappears above $T_2 = 59$ K when the system is still in the $\mathbf{q}_1$ CDW state. As shown in Fig. 4(a), the shoulder is still present at $T = 50$ K, while at 100 K $< T_1$ in Fig. 4(b) it is no longer detectable. We found no indication for a change in the energy scale, rather a loss of intensity above T_2. This makes a connection to the $\mathbf{q}_1$ CDW seem unlikely.

An interpretation of the modified dispersion as a CDW-related self-energy effect is analogous to the phenomenon known from electron-phonon coupling. It modifies the band mass below E_F in an energy window determined by the phonon modes. Above a cutoff energy ε_0 the band resumes its unaltered dispersion, as sketched in the inset of Fig. 3. This ''kink'' feature can be detected in ARPES [11,12,18]. However, the energy scale observed here is much larger than any phonon modes of $NbSe_3$, which are reported to be no higher than 30 meV [17,19]. One is thus led to attribute this effect to coupling of the electrons to another bosonic excitation mode of energy $\varepsilon_0 \approx 90$ meV. It is striking that within experimental error bars ε_0 coincides with the excitation gap $2\,\Delta_2^*$. The self-energy effect is observed in a band partially nested with the $\mathbf{q}_2$ instability, and the temperature dependence supports a connection to the $\mathbf{q}_2$ CDW phase.

The nature of an excitation process with cutoff energy $2\,\Delta_2^*$ needs closer consideration. Theoretical treatment of coupling between quasiparticles and excitations of the solid is a developing field, and we are left to review the various mechanisms. Collective excitations of the CDW condensate are too small in energy to be relevant [1]. Concerning intrinsic excitations such as, e.g., interband transitions, data for $NbSe_3$ are lacking. Optical data of other 1D systems [19] do not provide conclusive evidence for exciton states near the gap. Broadband optical data as well as a stringent theory describing such specific electron-electron coupling, however, have not come to the authors' attention.

Alternatively, self-energy effects can also be caused by the reduced phase space available for electron scattering that results from the large Fermi surface loss. Such analysis in the presence of phonons has been brought forward by Castro Neto [20]. It provides a good description of similar renormalization effects in $TaSe_2$ exceeding the phonon energy scale [21]. Our ARPES data on $NbSe_3$ suggest a relationship to the CDW instability, and provide independent evidence compatible with such a scenario. The exact nature of the self-energy contribution, however, which may involve coupling to phonons or electrons, cannot be revealed by this experiment alone and will require further exploration.

In summary, the ARPES data on the low-temperature state of $NbSe_3$ provide a k-resolved determination of CDW effects on the single-particle spectra. At nested parts of the Fermi surface we observe pseudogap behavior, and even in non-nested sections the Fermi edge is not fully restored. There, anomalous dispersions are suggestive of many-body coupling phenomena. The modified energy scale of the order of the excitation gap suggests a connection to the mechanism that drives formation of the CDW condensate.

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